

AD-A149 100

ON SHRINKAGE AND MOLECULAR EXTENSION(U) CORNELL UNIV
ITHACA NY DEPT OF MATERIALS SCIENCE AND ENGINEERING
D T GRUBB 20 DEC 84 TR-1 N00014-83-K-0471

1/1

UNCLASSIFIED

F/G 7/4

NL

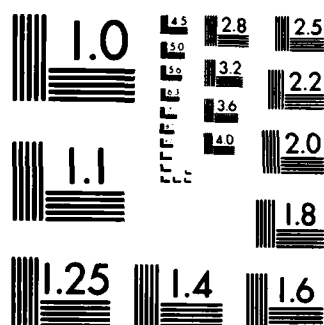


END

FILMED

DTIC





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A149 100

JUL 11 1983

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE and Subtitle On Shrinkage and Molecular Extension		5. TYPE OF REPORT & PERIOD COVERED Technical
7. AUTHOR(s) D. T. Grubb		6. PERFORMING ORG. REPORT NUMBER N00014-83-K-0471
9. PERFORMING ORGANIZATION NAME AND ADDRESS CORNELL UNIVERSITY Office of Sponsored Programs Ithaca, New York 14853		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 631-843
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, VA 22217		12. REPORT DATE December 20, 1984
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 9
		15. SECURITY CLASS. (of this report) Unclassified
15. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Accepted for Publication in J. Materials Science Letters		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Include: oriented polymer, network extension, shrinkage, retraction, molecular extension.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) When an oriented polymer is heated, it often retracts towards an isotropic state. The change in shape is a measure of the extension of the molecules in the oriented sample. The several different functions that have been used to define molecular extension are derived and reviewed. It is concluded that the ratio (oriented length/shrunk length) is the most appropriate, and that a direct test by neutron scattering would be feasible.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 55 IS OBSOLETE
S/N 0102-LF-014-6601

85 01 07 054

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0471

Task No. NR 631-843

TECHNICAL REPORT NO. 1

On SHrinkage and Molecular Extension

by

D. T. Grubb

Prepared for publication

in the

Journal of Materials Science, Letters

Cornell University

Department of Materials Science and Engineering

Ithaca, NY.

December 20, 1984

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.



A-1

On Shrinkage and Molecular Extension

D.T. Grubb
Department of Materials Science & Engineering
Cornell University
Ithaca, NY 14853

Many authors have been concerned with the shrinkage of oriented specimens which occurs when they are heated.¹⁻¹⁷ The earlier work dealt largely with crosslinked and other reversible systems, applying thermoelasticity and stress optical measurements to the study of networks and oriented crystallization under stress.¹⁻⁴ Later studies have concentrated on measuring shrinkage to help characterize the structure of the oriented sample.⁵⁻¹⁷ In particular, shrinkage should be directly related to the extension of molecules in the sample.

In recent papers Porter and coworkers^{13,14} defined a "molecular draw ratio", MDR, essentially by using the original undrawn state as reference. The purpose of this paper is to show that use of the final shrunk isotropic state as a reference state for the shrinkage gives a more logical and correct formula for molecular extension. It also allows comparison with systems where the "undrawn" state is inaccessible.

When an isotropic ideal rubber elastic material is deformed, the measured extension ratio λ in a given direction is identical to the extension ratio of the molecular network M . If the network is allowed to return to isotropy by removal of external stress or increase of temperature, the sample will recover completely, that is, it will return to its original dimensions. A cross-linked material which is glassy or partially crystallized may remain extended under zero stress, but will recover completely when the temperature is raised. Consider now a polymeric material that is not crosslinked, where the molecular network is made up of impermanent entanglements. When this material is deformed, the measured extension ratio is made up of two parts, reversible elastic extension of the molecular network and irreversible slippage and disentanglement. If the network is allowed

to return to isotropy only part of the deformation is recovered. Under these conditions, can the molecular network extension be determined, and how is it related to the measured lengths?

If the material is amorphous, measurement of x-ray orientation function and birefringence will give the degree of molecular orientation. However this does not allow the extension ratio of the molecular network to be determined unless the entanglement density is known. As disentanglement occurs during deformation^{9,18,19} the entanglement density is not known in general. If the material is semi-crystalline, the results of such experiments are even more difficult to interpret. X-ray results give the crystal orientation, and when the draw ratio is high, the orientation is almost perfect and differences between samples are difficult to distinguish. For these reasons, a relation between molecular extension and the measured lengths would be very desirable.

To be specific, consider a sample shown in Fig. 1, of original undeformed length L_0 which is extended by uniaxial tension to an extended length L_T . On heating to a temperature above the melting point of any crystals in the sample, it shrinks to an intermediate length, L_S , at which it is again isotropic. If both deformations are elastic, then we expect $L_S = L_0$, and molecular extension $M = L_T/L_0 = L_T/L_S$. If both deformations are elasto-plastic, then we cannot define M exactly, instead there are two inequalities: $L_T/L_0 > M > L_T/L_S$. If the initial drawing is elasto-plastic but the recovery is pure rubber elastic, a completely unconstrained relaxation, then $L_T/L_0 > M = L_T/L_S$. To be even more specific, let us take $L_0 = 1$, $L_T = 10$, $L_S = 3$ as a numerical example, and put the numerical result in parenthesis after the formula $M = L_T/L_S (=10/3)$. This seems very reasonable, but it requires detailed justification since the formulae used by Porter and coworkers^{13,14,17} are quite different.

Imagine the shrunken sample, length L_S , to be redrawn with no molecular slippage to L_T . Then an isotropic sample is being extended by extension ratio

L_T/L_S and recovering completely. The molecular extension ratio M will be identical to the observed extension ratio. This notional redrawing emphasizes that $M = L_T/L_S$ is equivalent to using the shrunk isotropic state as reference state to measure deformations. It also suggests that if M is associated with some physical reality of the extended sample, it must have the same value after each redrawing cycle, since there is no slippage. The more cycles of (isotropic $L_S \leftrightarrow$ extended L_T) the more difficult it is to see that some original (isotropic L_0) state from which the sample was irreversibly deformed can be relevant.

Surveying previous literature, most papers contain shrinkage data^{3-8,11,13,15,16} and shrinkage, S , is often thought to be self-evident and not defined. When it is defined, it is $(L_T - L_S)/L_T$ in the terms of Fig. 1. (0.7 in the numerical example) In Sattler's paper³ an extension, D , is defined as $1/(1-S) = L_T/L_S$ and in refs. 3 and 4 $1/(1-S)$ is used in place of λ in stress birefringence calculations. L_T/L_S is also sometimes called the contraction.^{2,7,8} The literature can be confusing, for in many cases, when the material is found as fibers from solution^{5,6,10-12} or supplied in an oriented form^{2-4,15} the "original unstretched length L_0 " is not applicable or available and the length of the fully oriented material is described as "original length". Thus in refs. 10 and 12 the function used is described as "length/original length" but this is equivalent to L_S/L_T . Some authors^{13,16} use "Recovery", R , which is defined as $(L_T - L_S)/(L_T - L_0) = S/(1 - 1/\lambda)$ (=7/9). This is the fraction of the original deformation which is recovered. Kahar et al.⁹ use different functions, as follows:

$$\lambda = L_T/L_0 \quad \epsilon = (L_T - L_0)/L_0 \quad (=9)$$

$$\lambda' = L_S/L_0 \quad \epsilon' = (L_S - L_0)/L_0 \quad (=2) \text{ (inferred from text ref. 9)}$$

$$\text{Shrinkage strain } \epsilon - \epsilon' = (L_T - L_S)/L_0 \quad (=7)$$

$$\text{residual strain } \epsilon'/\epsilon = (L_S - L_0)/(L_T - L_0) = 1 - R \quad (=2/9)$$

The use of nominal strains rather than extension ratios is due to the small deformations in this study of PMMA. The deformations could be fully recovered at high temperature and finite residual strains ($L_S > L_0$) were measured at lower temperatures.

This leaves the "molecular draw ratio" or MDR of Porter and co-workers previously mentioned as a reason for this paper. Three formulae are given for MDR; L_S/L_0 ($=3$) and $R \cdot L_T/L_0$ ($=7.77$) in reference 13 which is corrected in a corrigendum and in reference 14 to $\{(L_T - L_S)/L_0 + 1\}$ ($=8$). The first formula was presumably a typographical error of some sort. The second two are quite similar at high λ as they can be expressed as λR and $\lambda R + (1 - R)$. Neither was explained by the authors, but it is easy to create reasons for their use: λ is the extension ratio. R is the fraction of the deformation that is recoverable. Recoverable deformation comes from the molecular extension, so $MDR = \lambda R$. However, this is faulty since the extension ratio λ is mixed with deformation, or strains, since $R = (L_T - L_S)/(L_T - L_0) = (\frac{L_T - L_S}{L_0})/(\frac{L_T - L_0}{L_0})$ is a ratio of strains.

Modifying R to $R' = (\frac{L_T - L_S}{L_0} + 1)/(\frac{L_T - L_0}{L_0} + 1)$ which is a ratio of extension ratios, gives $R' = (L_T - L_S + L_0)/L_T$ ($= 0.8$) and so $\lambda R' = (L_T - L_S + L_0)/L_0$ ($=8$) which is the definition of MDR used in ref. 14. The critical feature in this derivation, easily passed over, is the choice of L_0 as the divisor for strain when the initial and final states are L_T and L_S . If L_S is chosen as the divisor, the reference length, then the modified R becomes

$$R'' = (\frac{L_T - L_S}{L_S} + 1)/(\frac{L_T - L_0}{L_0} + 1) = \frac{L_T}{L_S} \cdot \frac{L_0}{L_T} = L_0/L_S \quad (= 0.33)$$

and $\lambda R'' = L_T/L_0 \cdot L_0/L_S = L_T/L_S = M$ ($=3.33$).

As can be seen from the numerical example, the difference between these formulae for molecular extension can be very significant. Taking data from ref. 13, where $\lambda = 36$, $R = 0.51$, the calculated MDR was 18.4 and the correction of ref. 14 would bring that to 18.8. However, $M = L_T/L_S$ is 2.0. Such low values do not seem to be realistic for a material that has undergone a 36x deformation and has a modulus of 40 GPa.¹³ It seems much more likely that the shrinkage is not completely slippage free, that the contraction was hindered, and so $M = 2.0$ is only a lower limit. The correction in ref. 14 stated that by a change of procedure, R could be increased to 0.7 and several other authors have noted changes in shrinkage due to specimen thickness^{6,10} and heating conditions.^{6,7,13} Other sample types of high deformation ratios shrink almost completely back to their original length^{7,8,16,17} with $R \approx 0.98$.

For describing the state of a system, any functions of the state variables are equally valid. Thus when the calculated values of MDR are found to have a linear relationship to modulus in a particular set of samples²⁰, this is a valid correlation unaffected by the above arguments. But when a function is related to a particular physical property, here the extension of the molecular entanglement network, an independent measurement of the property determines the validity of the function.

Small angle neutron scattering of uniaxially oriented samples can give the molecular extension²¹, since the radius of gyration parallel to the draw direction $R_g(1)$ is proportional to molecular extension and the radius of gyration perpendicular to the draw direction $R_g(2)$ is proportional to (molecular extension)^{-1/2}. For affine deformation when network elements deform in the same way as the whole molecules, the network extension should be $(R_g(1)/R_g(2))^{2/3}$. Unfortunately the only available data²¹ refer to a case where the recovery was almost complete and then the differences between the $MDR = \{(L_T - L_S)/L_0 + 1\}$, and

the molecular extension suggested here, $M = L_T/L_S$ become very small, Table 1. SANS from samples where the recovery is 80% or less would clearly distinguish between the two formulae (Table 2). The difference is greater at greater draw ratios, since as $\lambda \rightarrow \infty$, $MDR \rightarrow \infty$ but $M \rightarrow 1/(1-R)$. Comparison of such shrinkage results with SANS would only be worthwhile if one could be sure that the retraction from the oriented state was purely elastic with no further slippage or disentanglement. Such slippage would cause L_S to be too high and M to be too low.

It should also be pointed out that measurement of entanglement density and its decline on drawing at high temperatures by use of birefringence data¹⁸ requires measurement of shrinkage.¹⁵ The molecular orientation and thus the birefringence depends on the entanglement density and the network extension. Without shrinkage measurement the only extension available is λ . Only if the deformation is fully reversible will this be the same as network extension.

Acknowledgements

This work was supported in part by the Office of Naval Research. I would also like to thank Professor Porter for supplying preprints of his work.

TABLE 1

Comparison of M and MDR with SANS results*

λ^*	MDR*	M [†]	SANS*
2.9	2.9	2.9	2.8
4.2	4.0	3.5	4.1
5.1	5.0	4.6	5.0
9.6	9.4	8.0	8.6

* Data from Table 1 of reference 21.

† $(\text{MDR}-1)/\lambda = 1-1/M$; $M = \lambda/(\lambda-\text{MDR}+1)$ Table 2

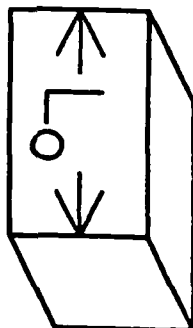
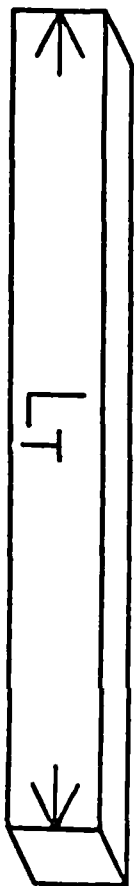
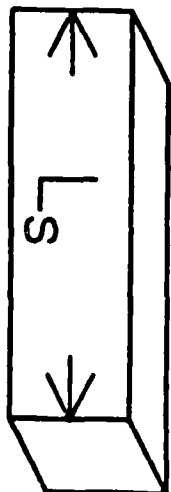
Comparison of M and MDR at lower recovery

λ	R	MDR*	M*
2	0.8	1.8	1.67
5	0.8	4.2	2.78
10	0.8	8.2	3.57
2	0.6	1.6	1.43
5	0.6	3.4	1.92
10	0.6	6.4	2.17

* $\text{MDR} = \lambda R + 1 = R$, $M = \lambda/(\lambda + R - \lambda R)$

References

1. Flory, P.J., J. Amer. Chem. Soc. 78, 5222, (1956).
2. Mandelkern, L., D.E. Roberts, A.F. Diorio and A.S. Posner, J. Amer. Chem. Soc. 81, 4148, (1958).
3. Sattler, G., Kolloid-Z. 187, 12, (1963).
4. Pinnock, P.R., I.M. Wood, Trans. Farad. Soc. 62, 1308, (1966).
5. Rijke, A.M. and L. Mandelken, J. Polymer Sci. A2 8, 225, (1970).
6. Pennings, A.J. and J.M.M.A. van der Mork, Rheol. Acta. 10, 174, (1971).
7. Barham, P.J. and A. Keller, J. Polym. Sci. Letters Edn. 13, 197, (1975).
8. Barham, P.J. and A. Keller, J. Mater. Sci. 11, 23, (1976).
9. Kahar, N., R.A. Duckett and I.M. Ward, Polymer 19, 136, (1978).
10. Grubb, D.T. and A. Keller, Colloid Polym. Sci. 156, 218 (1978).
11. Pennings, A.J. and A. Zwijnenburg, J. Polym. Sci., Polym. Phys. Edn. 17, 1011, (1971).
12. Grubb, D.T. and A. Keller, J. Crystal Growth 48, 321, (1980).
13. Watts, M.P.C., A.E. Zachariades and R.S. Porter, J. Mater. Sci. 15, 426, (1980).
14. Porter, E.S., M. Daniels, M.P.C. Watts, J.R.C. Pereira, S.J. DeTeresa and A.E. Zachariades, J. Mater. Sci. Letters 16, 1134 (1981).
15. Yamada, K., M. Kamezawa and M. Takanayagi, J. Appl. Poly. Sci. 26 49 (1981).
16. Cappaccio, G. and I.M. Ward, Colloid. Polym. Sci. 260, 46 (1982).
17. Wang, L.H. and R.S. Porter, J. Polym. Sci., Polym. Phys. Edn., 21 907 (1983).
18. Raha, S. and P.B. Bowden, Polymer, 13, 174, (1972).
19. Grubb, D.T. J. Polym. Sci. Polym. Phys. Edn., 21, 165, (1983).
20. Chuah, H.H. and R.S. Porter, to be published.
21. Hadziioannou, G., L.H. Wang, R.S. Stein and R.S. Porter, to be published.



DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Doude Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

ABSTRACTS DISTRIBUTION LIST, 356A

Naval Surface Weapons Center
Attn: Dr. J. M. Augl, Dr. B. Hartman
White Oak
Silver Spring, Maryland 20910

Professor Hatsuo Ishida
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Dr. Robert E. Cohen
Chemical Engineering Department
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. R. S. Porter
Department of Polymer Science
and Engineering
University of Massachusetts
Amherst, Massachusetts 01002

Professor A. Heeger
Department of Chemistry
University of California
Santa Barbara, California 93106

Dr. T. J. Reinhart, Jr., Chief
Nonmetallic Materials Division
Department of the Air Force
Air Force Materials Laboratory (AFSC)
Wright-Patterson AFB, Ohio 45433

Professor J. Lando
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Professor C. Chung
Department of Materials Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

Professor J. T. Koberstein
Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08544

Professor J. K. Gillham
Department of Chemistry
Princeton University
Princeton, New Jersey 08

Professor R. S. Roe
Department of Materials S
and Metallurgical Engir
University of Cincinnati
Cincinnati, Ohio 45221

Professor L. H. Sperling
Department of Chemical E
Lehigh University
Bethlehem, Pennsylvania

Professor Brian Newman
Department of Mechanics a
Materials Science
Rutgers University
Piscataway, New Jersey (

Dr. Adolf Amster
Chemistry Division
Naval Weapons Center
China Lake, California (

Dr. Stuart L. Cooper
Department of Chemical E
University of Wisconsin
Madison, Wisconsin 53706

Professor D. Grubb
Department of Materials S
and Engineering
Cornell University
Ithaca, New York 14853

Dr. D. B. Cotts
SRI International
333 Ravenswood Avenue
Menlo Park, California (

PLASTEC
DRSMC-SCM-0(D), Bldg 351
Armament Research & Deve
Center
Dover, New Jersey 07801

END

FILMED

2-85

DTIC

Troy, N

Profes:

Depart:

Prince:

Prince:

